**Development, Characterization,
and Evaluation of Materials for
Open Cycle MHD**

**Quarterly Report for the Period
October - December 1976**

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DEVELOPMENT, CHARACTERIZATION, AND EVALUATION
OF MATERIALS FOR OPEN CYCLE MHD

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1.0 OBJECTIVES

The objectives of this program are to develop, test, characterize, and evaluate materials for open-cycle, coal-fired MHD power generators. The specific immediate goals emphasize electrode and insulator materials, including: 1) the testing and evaluation of the enhanced effects of alkali seed on materials in a dc electric field; 2) the development and testing of improved electrodes and insulators with controlled microstructures, compositions and properties; and 3) the characterization and evaluation of materials relating to both the US MHD Program and the US-USSR Cooperative Program for MHD power generators.

2.0 SCOPE

The scope of this program encompasses the following areas:

- Reproducible laboratory testing of both ceramic and metal electrode materials and insulator materials in alkali seed/slag under dc electric current and voltages as functions of temperature, seed/slag, and composition.
- Development and fabrication of electrodes, insulators, and other related materials with controlled electrical, chemical, and physical properties, including evaluation in laboratory tests in US MHD test facilities and as part of the US-USSR testing program.
- Characterization and evaluation of materials tested under the US-USSR and the US MHD programs include the measurement and analysis of structural, chemical, and thermophysical properties of electrodes, insulators, slag, and other related materials before and after testing.

3.0 TECHNICAL PROGRESS

3.1 ELECTROCHEMICAL EFFECTS OF ALKALI SEED ON ELECTRODES AND INSULATORS

Alkali metal seed and high electric current density pose two severe synergistic conditions for electrodes and insulators in the channel of open-cycle, fossil-fueled MHD power generators. Recent long-time tests of

a US materials channel in the USSR (U-02 Phase I)(1,2) have shown that potassium penetration can be extensive in both electrodes and insulators and that the presence of a dc electric field and current can substantively enhance these effects.

To illustrate the overall effects, the microstructure of both the cathode and anode of a $0.78\text{CeO}_2 \cdot 0.20\text{ZrO}_2 \cdot 0.02\text{Ta}_2\text{O}_5$ electrode material are compared, Figures 1 and 2. This electrode pair had been tested in the U-02 (Phase I) for 98 hr at 1 A/cm^2 with a surface temperature of $\sim 1700^\circ\text{C}$. Note the extensive penetration and reaction of the potassium carbonate (dark black in the micrograph) with the cathode and the porous MgO . This penetration ultimately resulted in gross degradation of the electrode system.

The degree of penetration and reaction of the potassium with the electrodes, in particular the cathode, increases with increases in the current density. The microstructure of a cathode tested at $\sim 0.5 \text{ A/cm}^2$ for 98 hr (Figure 3) shows substantially less seed penetration than one which was conducted $\sim 1 \text{ A/cm}^2$ for identical times and temperatures (Figure 2). At these temperatures the seed in this and other electrodes tested have altered the composition, reacting to form a new phase in some electrodes, and penetrating the electrodes and insulators by diffusion and through the open pores. After testing, the potassium carbonate has hydrated. The degree of penetration and reaction varies between materials and will be dependent upon the composition, structure and fabrication of each electrode and insular. Other factors, such as the state of seed either as gas, liquid, solid compound, or dissolved in slag, will influence these effects.

3.1.1 Testing Procedures

An engineering-type laboratory test is being developed for evaluating potential electrodes and insulators in the presence of both potassium seed/slag and an applied dc electric current and field. The test system being developed will be able to vary the temperature to 1600°C , the seed concentration and composition, and dc current and field. The ultimate test system should be relatively simple, provide reproducible results, and be representative of actual or simulated MHD material test results.

Two preliminary test methods have been developed. These methods are described and some initial results will be described later.

3.1.1.1 Test Configuration 1

A schematic of test configuration 1 is given in Figure 4. The sample, a cathode (or anode depending on external electrical circuitry) and a control (no electrical current) are suspended by platinum (Pt) wire in a molten potassium salt bath. The Pt crucible holding the molten salt is connected to the other electrical lead resulting in the crucible being the anode (or cathode).

The molten salt can be any molten potassium system. Initial studies used K_2SO_4 , although K_2CO_3 or potassium containing slag could be tested. Sufficient powder is melted in the Pt crucible to obtain the desired molten salt level. After cooling to ambient temperature, the salt is placed in the test chamber. The assembly containing the electrode and control is lowered

FIGURE 1. Microstructure of $0.78\text{CeO}_2 \cdot 0.20\text{ZrO}_2 \cdot 0.02\text{Ta}_2\text{O}_5$ Cathode, U-02 Phase I. Tested for 98 hr at $\sim 1 \text{ A/cm}^2$.

FIGURE 2. Microstructure of $0.78\text{CeO}_2 \cdot 0.20\text{ZrO}_2 \cdot 0.02\text{Ta}_2\text{O}_5$ Anode, U-02 Phase 1. Tested for 98 hr at $\sim 1 \text{ A/cm}^2$.

FIGURE 3. Microstructure of $0.78\text{CeO}_2 \cdot 0.20\text{ZrO}_2 \cdot 0.02\text{Ta}_2\text{O}_5$ Cathode, U-02 Phase I. Tested for 98 hr at $\sim 0.5 \text{ A/cm}^2$.

FIGURE 4. Schematic of Test Configuration 1

into the test assembly until it is within 2.5 cm of the molten potassium salt. The furnace is then slowly heated to the test temperature. At temperature, the assembly is lowered until the electrode and control are submerged ~0.32 cm into the bath. An external electric field is applied until the current is at the required level. During the test the electric fields are manually adjusted to maintain a constant current.

3.1.1.2 Test Configuration 2

A schematic of test configuration 2 is given in Figure 5. In this configuration, the test assembly has both the anode and cathode as well as a control. All other parameters remain the same as in test configuration 1, except the current passes from the cathode to the anode, and the Pt crucible is not used as an electrode.

Substantial difficulty has been encountered using both configurations because of the vapor loss of the K_2SO_4 or K_2CO_3 which condenses on and/or reacts with the heating elements and refractory components of the furnace. This has resulted in periodic furnace failure.

The potassium has also reacted slowly with the Al_2O_3 hardware, and other insulators are being evaluated.

3.1.2 Results

Some initial tests were conducted using $0.75 MgAl_2O_4 \cdot 0.25 Fe_3O_4$ spinel and $La(Mg)CrO_3$ electrode materials tested in the US-test in U-02 Phase II. These preliminary results are described.

3.1.2.1 Test 1: $0.75MgAl_2O_4 \cdot 0.25Fe_3O_4$

A $0.75MgAl_2O_4 \cdot 0.25Fe_3O_4$ spinel cathode (S-121-A) and control (S-121-B0) was tested using configuration 1. These spinel samples were sibling samples to those used in the US Phase II test in the USSR. The fabrication and properties of these electrodes are described in subsequent sections of this report (3.2 and 3.3). The 88.8% Theoretical Density (TD) electrodes were cut into test samples with rectangular cross sections, 0.32 cm x 0.31 cm x 3.16 cm. A hole was drilled in one end of each sample and a platinum wire attached.

The test was conducted in air with the K_2SO_4 at $1300^\circ C$ for 90 min with a current of 1 A, equivalent to a current density of $\sim 10 A/cm^2$. This is a very high value and was inadvertently applied. In addition, the electrochemical effects may have also affected the control sample. The applied voltage at the start of the test was 38 V, but increased during the test to 90 V at the end of the test. The test was terminated when the electrical systems became open circuit.

FIGURE 5. Schematic of Test Configuration 2

The sample and sample assembly after the test are shown in Figure 6. The control sample remains intact and attached to the Pt wire. The bottom 0.6 cm is missing and approximately one-third of the surface is covered with K_2SO_4 . The cathode had broken from the Pt wire and was located in the bottom of the crucible. Pieces of the cathode are shown in Figure 7 and appeared as a worm-like rod, which had enlarged significantly in length. The material was friable, and pieces placed in room-temperature water separated into small pieces, approximately the same size as the original grains of the spinel. The section which fell from the control (S-121-B0) could not be discerned from the cathode pieces (S-121-A).

The control sample was mounted and prepared for ceramographic examination. Polishing and cutting are performed in nonaqueous media. The microstructure of this cross-section shows extensive degradation in the portion submersed in the molten K_2SO_4 , (Figure 8). That portion not in contact with the K_2SO_4 remained relatively intact. Potassium sulfate deposits (they appear as dark areas in micrographs) are found principally in the reacted area near the bottom of the sample, which was in contact with the molten salt. However, smaller amounts coat the sides of the sample above the reacted area and in the hole used to connect the Pt wire to the sample.

The potassium in the hole also contains particles of Pt, presumably from the Pt paste used to coat the hole prior to attaching the Pt current leadout. A Pt reaction layer, ~ 0.003 cm thick, was formed between the paste and the oxide surface, (Figures 9 and 10). The microstructure suggests a chemical attack and not erosion by the K_2SO_4 . The result is a breakup of the spinel surface into small pieces which are entrapped in the solidified K_2SO_4 , Figure 10.

The $0.75MgAl_2O_3 \cdot 0.25Fe_3O_4$ electrode has also fractured along the boundaries of the large grains throughout the relatively unreacted portion of the control sample. The attack proceeds along the grain boundaries but appears to be more pronounced when the grain boundaries intersect the sample surfaces. This enhanced reaction appears to be related to the reaction of the potassium seed with the microphase which is found at the grain boundaries of the spinel. (See Section 3.3 on U-02 Phase II characterization.) Such reaction could be the cause of the failure along the grain boundaries and loss of structural integrity.

A second phase is also observed in the spinel grains. This slightly darker, needle-like phase is located in the interior of the grains and appears to originate from the internal interfaces such as boundaries or pores. This phase is very similar to second phases observed in the preliminary evaluation of similar electrodes tested as part of the U-02 Phase II test. This phase is depleted in iron, enriched in aluminum, and contains potassium but no sulfur.

FIGURE 6. Post-test Sample Holder with Control Sample, Test 1;
($0.75 \text{ MgAl}_2\text{O}_4 \cdot 0.25 \text{ Fe}_3\text{O}_4$; Test Configuration 1)

FIGURE 7. Post-test Cathode After Test 1

FIGURE 8. Transverse Cross-Section of Control Sample (S-121-B0), Test 1

0.2 mm

FIGURE 9. Platinum Reaction Layer at Top of Control Sample (S-121-B0), Test 1

0.1 mm

FIGURE 10. Interface Between Reacted and Unreacted Zone of Control Sample (S-121-B0). See also Figures 8 and 9.

3.1.2.2 Test 2: $0.75\text{MgAl}_2\text{O}_3 \cdot 0.25\text{Fe}_3\text{O}_4$

The test of another $0.75\text{MgAl}_2\text{O}_3 \cdot 0.25\text{Fe}_3\text{O}_4$ cathode (S-121-C) and control (S-121-D0) was also conducted at 1300°C in K_2SO_4 in configuration 2, but with a lower electric current density. The cathode obtained from the same electrode as that of Test 1 was $0.33\text{ cm} \times 0.30\text{ cm} \times 3.17\text{ cm}$. The time, current and voltage are tabulated in Table 1. The current density based on the cross-sectional area was 3 A/cm^2 . The electric potential required to maintain a constant current decreased from 19 V at the start of the test to 4.2 V after 1440 min when the test was terminated. The cathode and control samples are shown in Figure 11. The control sample in Figure 11 is touching the cathode and frozen in place with solidified potassium sulfate.

The platinum crucible had developed a hole in the side, apparently caused when the cathode touched the crucible wall, melting the platinum by ohmic heating. The test was terminated as the K_2SO_4 flowed from the hole, lowering the liquid level below the cathode.

The transverse metallographic sections of the midplane of the cathode and control are shown in Figure 12. The dark phase of K_2SO_4 covers most of the cathode's external surface. The large metallic phase in the K_2SO_4 at the upper end of the sample is platinum wire and paste, which are used to support the sample. The K_2SO_4 at the upper portions of the cathode also contains smaller pieces of platinum which probably came from the paste. Many of the dark deposits inside the sample also contain K_2SO_4 , and K_2SO_4 also coats the outside surfaces of the sample.

Over 80% of the sample has been altered microstructurally during the test. The top 20% has been altered the least. An example of the resulting microstructure from the reactive zone is shown in Figure 13. The zone is located 1.4 cm from the bottom of the sample and 0.18 cm in from the side. The dark phase is both porosity and potassium salt. Two other phases are also observed. The first phase is light colored and appears to be the original spinel matrix. The second phase is darker than the matrix but lighter than the K_2SO_4 . This phase is acicular in morphology, Figure 14, and is similar to that observed in the central sample of Test 1 (see Section 3.1.2.1).

An X-ray spectrum elemental analysis of the light-colored phases identified the major elemental species as magnesium, aluminum, and iron with compositions of the original spinel. The medium dark acicular phases contained potassium with a depletion in magnesium and a concentration of aluminum and iron. The analysis of the grain boundaries where potassium is concentrated shows high concentrations of both potassium and sulfur with minor amounts of iron and aluminum, with some silicon. The iron concentration in this grain boundary reaction layer is higher in the interior of the cathode than in the reaction layer at grain boundaries nearer the sample surface. A summary of the elemental analysis is given in Table 2.

TABLE 1. Test 2 Operating Conditions

<u>Time, min</u>	<u>Electric Current, A</u>	<u>Electric Potential, V</u>
0	0.3	19.0
30	0.3	12.0
60	0.3	10.0
90	0.3	8.8
120	0.3	8.0
1080	0.3	5.0
1110	0.3	5.0
1170	0.3	4.8
1230	0.3	4.6
1290	0.3	4.4
1350	0.3	4.3
1410	0.3	4.2
1440	0.3	4.2

FIGURE 11. Post Test Sample Assembly with Cathode (S-121-C) and Control (S-121-D0)

FIGURE 12. Transverse Cross-Sections of Cathode (S-121-C) and Control (S-121-D0), Test 2

TABLE 2. X-ray Spectrum Elemental Analysis for Cathode of Test 1

<u>Phase No.</u>	<u>Relative Color</u>	<u>Major Components</u>	<u>Minor Components</u>	<u>General Location And Description</u>
1	Dark	K, S	Fe>>Al, Mg	On outside surface of sample, internal open porosity and some grain boundaries.
2	Light	Ag, Al, Fe		Original matrix
3	Medium dark	Al, K	Fe	Acicular growth from grain boundaries and porosity.
4	Very light	--	--	Acicular growth found in areas where phase 3 is located.
5	Light dark	Fe, Mg		Found only on control surface, see Figure 14.

The sulfur is only associated with the potassium. Sulfur on the interior of the samples is found in the open grain boundaries and pores. No sulfur is found in the interior of the grains.

The control sample (S-121-D0) showed significantly less interaction with the potassium than the cathode, Figure 12. The sample was not coated with K_2SO_4 , although some K_2SO_4 was found on the sample immediately above the initial level of the molten K_2SO_4 . The reaction zone appears to correspond to that area which had been in direct contact with the molten K_2SO_4 and near the area where this control sample had contacted the cathode. This reaction area also contained the same four phases observed in the cathode, although the extent of the reaction was less.

The very light acicular (unidentified Phase 4 in Table 2) is only associated with those areas which have a high concentration of the dark acicular structure (high in aluminum and potassium) as shown in Figure 15.

Another phase (Phase 5 in Table 2) was observed only on the sample surface next to the K_2SO_4 about one-third the distance from the bottom of the sample (Control A in Figure 12), Figure 16. This phase is an oxide of magnesium and iron, with no potassium, aluminum, or sulfur.

3.1.2.3 Test 3: $La(Mg)CrO_3$

A $La(Mg_{0.05}Cr_{0.95})O_3$ hot pressed sample prepared by General Refractories was tested in configuration 2. The cathode (GR-1), anode (GR-2), and control

FIGURE 13. Reaction Zone in Cathode (S-121-C), Test 2

FIGURE 14. Multiphase Region in Large Grains, Inside Reaction Zones

FIGURE 15. Microstructure of Control (S-121-D0), Test 2

FIGURE 16. Microstructure of Area One-Third the Distance from the Bottom of Control (S-121-D0), Test 2 (see Figure 12)

(GR-3) were parallelepiped with nominal dimensions of 0.31 cm x 0.32 cm x 3.61 cm. The test was conducted in air at 1300°C for a total of 1185 min, but was terminated because of furnace failure. The details of the test are given in Table 3. The current of 0.3 A corresponds to a current density of 2.76 A/cm² and 3.0 A/cm² for the anode and cathode, respectively.

The samples were lowered an additional 0.3 cm further into the molten K₂SO₄ after 185 min because of continued increase in voltage with time.

The electrodes samples had undergone extensive degradation during the test, Figure 17. Only the anode remained intact. The control was missing and only ~0.5 cm of the cathode remained. In addition, the test assembly fabricated from Al₂O₃ had expanded on the side of the anode, causing the observed distortion. The anode had apparently contacted the platinum crucible during operation, resulting in a hole in the crucible and a loss of half of the molten salt. The potassium salt which flowed through this hole apparently caused malfunction of the furnace and the termination of the test. The samples were kept at ambient temperatures and in air for 24 hr, after which time spalling occurred on the surfaces of the anode, Figure 17.

TABLE 3. Test 3 Operating Conditions

<u>Time, min</u>	<u>Electric Potential, V</u>	<u>Electric Current, A</u>	<u>Remarks</u>
0	3.5	0.3	
30	3.5	0.3	
60	40.0	0.3	
90	43.0	0.15	
120	50.0	0.07	
150	50.0	0.05	
185	3.0	0.3	Repositioned samples
210	2.8	0.3	
220	27.5	0.3	
1170	28.0	0	
1185	--	--	off

3.2 FABRICATION DEVELOPMENT

3.2.1 Fabrication of Magnesium-Aluminum-Iron Spinel

The severe environments of the open-cycle, coal-fired MHD channel require high-temperature, refractory ceramic electrodes which 1) have good thermal shock resistance, 2) are resistant to penetration and chemical attack

FIGURE 17. Post Test Electrodes and Assembly of GR-1, GR-2, and GR-3, Test 3

by potassium seed and combustion products, and 3) have a reliable attachment of the electrode to the metal current leadout. Most ceramic oxides exhibit poor thermal shock resistance, and in an effort to improve this resistance they are often fabricated with lower densities, having large dense particles surrounded by small particles, and then densified and strengthened by sintering or hot pressing. Although the thermal shock resistance can be improved in this manner, the vacancies in the structure principally represent open porosity.

This open porosity provides relatively easy paths for the transport and penetration of the vapor and liquid potassium compounds, e.g., K_2SO_4 , K_2CO_3 . Transport through the open pores is significantly easier than through the grain boundaries or bulk material where, for example, potassium ions can diffuse. In the open pores, not only ions can diffuse, but also vapor or liquid potassium compounds. Such movement is greatly enhanced on the cathode wall because of the negative charge attraction to potassium ions or ionic compounds.

The need for a low-density, open structure with high open porosity to increase thermal shock resistance conflicts with the need for a high-density material to resist seed penetration. The purpose of this study was to develop

methods to fabricate electrode materials with the porosity needed to improve the thermomechanical properties, yet no open porosity which would make the materials susceptible to seed penetration. Because of the interest in 0.75 MG $\text{Al}_2\text{O}_4 \cdot 0.25 \text{Fe}_3\text{O}_4$ spinel as an electrode, procedures were developed for fabricating this spinel with lower density below 90% TD, but with essentially closed porosity. Using this technique, electrodes were fabricated for testing in the US-USSR U-02 materials program under Phase II.

The fabrication procedures were based upon preliminary studies⁽³⁾ of small samples, which indicate that the 87 to 88% TD spinel can be fabricated with open porosities of less than 0.1%. It was also necessary to fabricate crack-free electrode sections $\sim 3.25 \times 1.5 \times 1.3$ cm. In addition, the back or cold surface layer (~ 0.025 cm thick) contained a >25% open porosity which might be more easily brazed or soldered to the metal current leadouts.

3.2.1.1 Powder Preparation

The 0.75 MG $\text{Al}_2\text{O}_4 \cdot 0.25 \text{Fe}_3\text{O}_4$ ^(a) was prepared with recrystallized alums, heat treated in air for 6 hr at 1290°C and 8 hr at 1475°C. It was crushed, ballmilled, and screened (-200, +325 mesh) prior to use at PNL. The powders from different batches often sintered differently. This was eventually traced to variations in the moisture content, the solution to which will be described later.

Controlled porosity and microstructures are obtained by introducing an organic pore former of controlled size and concentration. Sterotex (2 wt%) was homogeneously mixed with the spinel powder by ball milling for 1 hr with Al_2O_3 balls. The powder mixture is then stored in water-saturated air at room temperature for 24 hr.

The powder is pre-slugged at $\sim 525 \text{ kg/cm}^2$, then screened to -40 mesh. This is then placed in a rectangular steel die. To provide the high open porosity layer on the back surface, a uniform layer of spinel containing 20 wt% sterotex was added to the top surface. This was cold pressed at $\sim 840 \text{ kg/cm}^2$ to a green density of $\sim 60\%$ TD.

The compacts were sintered in air for 4 hr at 1600°C, with controlled, slow heating rates, especially at the low temperatures where the organic additions must decompose, vaporize, and be eliminated from the green compact.

The structure of a representative electrode prepared for the U-02 Phase II is illustrated in Section 3.3, Figures 27 and 28.

The resultant spinel structure is large grained, with grains approximately 0.02 cm in diameter. The impurities present in the original starting powder (see Table 4 in Section 3) are located principally at the grain

(a) Transtech, Gaithersburg, MD

boundaries. This second phase is principally a Ca-Si oxide with some iron. The pores are located uniformly throughout the electrode and vary in size. The pore diameters fall into two general sizes, $0.8-4 \times 10^{-5}$ cm and $1-2 \times 10^{-3}$ cm. The smaller sizes appear to be related to the original porosity of sintering while the larger pores probably relate to the pores formed by the organic additive.

3.2.2 Fabrication of Iron Aluminum Spinel Electrodes

Fabrication of $0.75 \text{ FeAl}_2\text{O}_4 \cdot 0.25 \text{ Fe}_3\text{O}_4$ hercynite-magnetite spinel electrodes for U-02 Phase II testing were hot pressed at Los Alamos Scientific Laboratory. Difficulties were encountered in fabricating quality electrode materials by conventional sintering methods. For this reason, hot pressing methods were used to fabricate electrodes for the U.S. Phase II test in the USSR U-02.

Two hercynite-magnetite powders, a and b, were used for hot pressing. Both were provided by Massachusetts Institute of Technology, but were made in different batches. Initial hot pressing tests of each powder gave different results with substantial cracking of the sample. The hot pressing conditions required to obtain a sample density of 4.37 g/cm³ were different for each powder. Since characterization and analyses of these powders were not performed, the reasons for these differences could not be determined. However, two compacts were successfully hot pressed for use as electrodes in U-02 Phase II. Pressing was done in graphite dies (4.45 cm in diameter) using 0.13-mm-thick grafoil and 0.05-mm-thick platinum liners for the die and punch faces. Powder was hot pressed at 1300°C and 34.5 MPa for one hour to promote homogenization and/or solid solution formation. Cracking in the initial tests was thought to result from the presence of two phase thermal expansions with different phase material. The density of the resulting compact was 4.54 g/cm³ or about 95.5% of the assumed 4.75-g/cm³ theoretical density with only one large crack. Four electrode sections were obtained for testing in the U-02 Phase II test. The microstructure and analyses of these electrode materials are discussed in Section 3.3 of this report.

The second hot pressing of electrodes for U-02 Phase II used a blend of 17 wt% powder a and 83 wt% powder b. This was hot pressed at 1385°C for 1 hr at 34.5 MPa, but the resulting density was only 4.38 g/cm³ or only 92.2% TD with some cracking. It appeared that the powder b could not be hot pressed successfully.

3.2.3 Refractory Capped Electrodes with Metal Current Leadouts

Graded electrodes with a refractory oxide cap, electronic electrode, and metal current leadout are being fabricated as part of the U.S. effort to develop a hot electrode for the U.S. channel test in the USSR U-25 MHD generator. Three graded configurations will be hot pressed by an industrial company using a continuous hot pressing facility: 1) $0.08 \text{ Y}_2\text{O}_3 \cdot 0.10 \text{ CeO}_2 \cdot 0.88 \text{ HfO}_2$ refractory cap on a $0.75 \text{ MgAl}_2\text{O}_4 \cdot 0.25 \text{ Fe}_3\text{O}_4$ electrode graded into

a titanium metal current leadout; 2) $0.8 \text{ Y}_2\text{O}_3 \cdot 0.10 \text{ CeO}_2 \cdot 0.8 \text{ ZrO}_2$ cap on a La(Mg)CrO_3 electrode graded into a titanium metal current leadout; 3) $0.12 \text{ Y}_2\text{O}_3 \cdot 0.88 \text{ ZrO}_2$ cap on a La(Mg)CrO_3 electrode graded into a titanium metal current leadout. These electrodes will be bonded to a copper or stainless steel base and tested at the MIT MHD test facility.

The preliminary results are encouraging. Although there is some cracking in the ceramic-metal layers, and some reaction between the metal and the electrode material, the bonding between the refractory cap and electrode can be achieved. Bonding with the La(Mg)CrO_3 was better than with the spinel. In an effort to reduce the reactions between the titanium and the oxide electrode, alloys of Mo/Fe and Ti/Mo are being evaluated. Electrodes with thinner ceramic-to-metal current leadout area or with no metal at all are being investigated.

Microstructures of some preliminary test samples, $\text{Y}_2\text{O}_3\text{-ZrO}_2/0.75 \text{ Mg Al}_2\text{O}_4 \cdot 0.25 \text{ Fe}_3\text{O}_4/\text{Mo-Fe}$ and $\text{CeO}_2\text{-Y}_2\text{O}_3\text{-HfO}_2/0.75 \text{ Mg Al}_2\text{O}_4 \cdot 0.25 \text{ Fe}_3\text{O}_4/\text{Mo-Fe}$, are illustrated in Figures 18 and 19 in Section 3.3.3.

3.3 PRETEST CHARACTERIZATION OF ELECTRODES AND INSULATORS FOR U-02 PHASE II

The electrode and insulator materials used in the U.S. module for the USSR U-02 Phase II Test were characterized and evaluated. The characterization included a spectrochemical and atomic absorption analyses of some starting powders, fabricated electrodes, and insulators; determination of melting points as required; microstructural analysis by optical and scanning electron microscopy and electron microprobe analysis; thermal physical property evaluations which include thermal expansion, thermal diffusivity and calculated thermal conductivity.

3.3.1 Chemical Analysis

3.3.1.1 Spectrochemical Analysis

The purity of the electrode and insulators for the U-02 Phase II channel was measured on sibling samples by spark source spectro-chemical methods. Also included are some starting powders. All elements are reported except rhenium and indium, which were internal standards, and oxygen, nitrogen, and carbon, which cannot be measured. All other elements not reported are $<0.1 \text{ at\%}$. These data are tabulated in Table 4.

3.3.1.2. Electrode Composition

The composition of the fabricated electrodes was determined using atomic absorption methods. These results are shown in Table 5.

TABLE 4. Spectrochemical Analyses of Insulator and Electrode Materials

Element	MgO		0.5CeO ₂ ·0.5ZrO ₂	3Mg Al ₂ O ₄ ·Fe ₃ O ₄				3FeAl ₂ O ₄ ·Fe ₃ O ₄			La(Mg)CrO ₃		
	85%	90%		E0 Starting Powder	KO Starting Powder	#83 Electrode BNW	#130 Electrode BNW	Trans. Tech. Electrode	Starting Powder MIT Electrode	MIT Electrode	La _{0.95} Mg _{0.05} CrO ₃ (Westinghouse)	LaMg _{0.05} Cr _{0.95} O ₃ (Gen. Refr.)	
Ce	40	20	-	0.39	0.15	0.83	0.58	76	1.9	280	63	31	
La	48	24	370	0.47	1.7	18	47	680	0.21	440	-	-	
Ba	1.2	0.77	174	54	14	54	14	45	1.4	4.4	17	8.7	
Zr	31	13	-	30	30	30	13	29	5.8	340	24	24	
Y	2.2	3.0	12	23	11	23	23	6	0.11	2.1	2.1	1.2	
Sr	1.1	1.1	11	7.3	3.7	3.7	16	13	3.5	13	19	56	
Ga	1.4	6.1	1.6	15	13	13	8.7	24	15	23	11	5.6	
Zr	22	38	76	17	24	19	56	95	23	94	24	13	
Cu	2.9	38	4.8	28	84	28	56	48	12	5.7	9.7	4.8	
Ni	0.3	0.4	3.1	55	280	55	550	190	27	19	14	7.9	
Fe	760	140	59	-	-	-	-	-	-	-	420	370	
Mn	8.4	4.2	6.6	~1200	210	62	310	650	170	78	11	1.4	
Cr	16	9.9	<13	12	730	35	730	750	34	130	-	-	
Ti	5.7	4.5	12	5.5	12	7.3	7.3	14	7.1	14	10	12	
Ca	260	124	430	150	170	150	220	260	33	110	120	200	
K	4	79	51	6	6	3.4	3.4	<1.9	>1%	3700	22	17	
Cl	5.6	450	52	5.1	12	5.1	2.4	12	23	24	20	10	
S	11	11	21	10	24	10	8	17	2300	810	8.6	15	
P	7.1	16	26	40	71	20	40	23	19	310	43	32	
Si	65	190	2500	490	980	980	2100	820	940	-0.5%	4300	1500	
Al	<1%	<1%	1%	-	-	-	-	-	-	-	<1%	<1%	
Mg	-	-	2400	-	-	-	-	-	170	1700	-	-	
Na	7.3	73	170	18	14	18	37	31	41	34	300	34	
F	86	300	130	54	2.5	13	450	35	24	80	120	120	
B	18	24	19	1.2	2.3	3.9	41	23	2.2	46	14	31	
Li	<0.15	0.83	17	16	22	65	<0.18	110	4.1	21	7.5	15	

Other Elements		Pb 7.2	Mo 1.3	Bi 32	Co 7	Co 14	Co 2.3	Mo 3.6	Pr 1.9	Sb 1.7	Hf 18	Pb 1.1	Sm 1.1
		W 11	V 5.2	W 8.6	V 1.1	V 8.5	V 4.3	Co 25	Cs 1.7	Sn 2.2	Nd 2.3	W 8.7	Nd 19
				Pr 57				V 5.7	Sn 2.2	Co 13	Mo 1.4	Nd 17	Pr 8.1
				Sn 5.2					Mo 2.5	V 5.5	Nb 1.8	Pr 6.1	Cs 3.2
				Nd 95					Co 4.4		Co 3.6	Cs 6.5	Mo 1.2
				Pb 21					V 7.3		V 2	Mo 1.2	Nb 3.1
				Pt 4.8							Sc 1.1	Co 3.1	V 4.0
				Ta 3.4									
				Hf <1%									

All Others <1 ppm

TABLE 5. Composition of Phase II, U-02 Channel
Electrodes and Insulators

Nominal Composition	Atomic Percent							
	Fe	Mg	Al	Cr	Zr	Ce	La	O
MgO		48.7						51.3
MgO		41.3						58.7
0.75FeAl ₂ O ₄ ·0.25Fe ₃ O ₄ (LASL)	26.7		25.3					48.0
0.75FeAl ₂ O ₄ ·0.25Fe ₃ O ₄ (MIT)	14.0		28.6					57.4
CeO ₂ ·ZrO ₂					25.2	24.9		49.9
0.75MgAl ₂ O ₄ ·0.25Fe ₃ O ₄	11.7	11.1	29.7					47.5
La _{0.95} Mg _{0.05} CrO ₃ (W)		3.5		22.6			16.8	57.0
LaMg _{0.05} Cr _{0.95} O ₃ (GR)		2.1		24.6			17.9	55.5

For the electrodes, these compositions correspond to something different from the reported nominal compositions. Although it is difficult to determine the actual composition, the above data suggest the following compositions:

- 0.75Fe Al₂O₄·0.25Fe₃O₄ (LASL):Fe_{6.33} Al_{6.0} O_{11.38} or 0.75Al₂O₃·0.25Fe_{6.33} O_{2.38} suggesting oxygen deficiency;
- 0.75Fe Al₂O₄·0.25Fe₃O₄ (MIT):Fe_{2.95} Al_{6.00} O_{12.04} or 3Fe Al₂O₄ suggesting lack of Fe₃O₄;
- 0.75Mg Al₂O₄·0.25Fe₃O₄:Mg_{2.25} Al_{6.00} Fe_{2.37} O_{9.61} or 2.25MgO·3Al₂O₃·0.79Fe₃O₄ but with a lack of oxygen;
- La_{0.95} Mg_{0.05} CrO₃ (W):La Mg_{0.21} Cr_{1.35} O_{3.4} or La Mg_{0.05} Cr_{0.95} O₃·Mg_{0.16} Cr_{0.4} O_{0.04} with an excess of Cr and Mg; and
- La Mg_{0.05} Cr_{0.95} O₃ (G.R.):La Mg_{0.12} Cr_{1.37} O_{3.11} or La Mg_{0.05} Cr_{0.95} O₃·Mg_{0.07} Cr_{0.42} O_{0.11} which also shows an excess of Mg and Cr.

3.3.2 Melting Points

Melting points of the electrode materials were determined in an electric tungsten "V" filament furnace⁽⁴⁾ in a purified argon atmosphere near atmospheric pressure. A small (10 to 25 mg) sample of the oxide was placed in the bottom of the filament. Melting was observed and temperatures measured simultaneously with a micro optical brightness pyrometer. The time required to measure a single melting point (of congruently melting oxide) was less than 5 seconds. The temperature measurement system was calibrated

by melting materials of known melting points, Cu, Fe and Al_2O_3 , resulting in a linear relationship between the true and measured temperatures. Three measurements were made for each of the reference materials of known melting points and three to five measurements for each electrode material. A least squares equation was obtained for the measured and real temperatures of the materials with known melting points. This fitted the data with a coefficient of determination of 0.9999. An average value of the measured melting temperatures was determined and the reference equation used to calculate the actual melting point.

The melting points of the Phase II electrode materials are given in Table 6. along with the arithmetic deviation for each oxide.

TABLE 6. Melting Points of Phase II U-02 Electrode Materials

Materials	Melting Point
$0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$	1) 1863 $\pm$ 8°C 2) 1851 $\pm$ 5°C
$0.75\text{FeO} \cdot \text{Al}_2\text{O}_3 \cdot 0.25\text{Fe}_3\text{O}_4$	1)(a) 1568 $\pm$ 5°C raising to 1730 $\pm$ 5°C (noncongruent) 2)(b) 1616 $\pm$ 10°C raising to 1720 $\pm$ 10°C with possible third step at 1600°C (noncongruent)
$\text{La}_{0.95} \text{Mg}_{0.05} \text{CrO}_3$	1)(c) 2234 $\pm$ 5°C

- (a) Hot pressed at Los Alamos Scientific Laboratory
(b) Hot pressed at Massachusetts Institute of Technology
(c) Westinghouse

The $0.75\text{Mg} \cdot \text{Al}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ (hercynite-nognitite spinel) and $\text{La}_{0.95} (\text{Mg})_{0.05} \text{CrO}_3$ melted congruently with distinct solid-to-liquid transformations. Conversely, the $0.75\text{Fe} \cdot \text{Al}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ electrode materials melted incongruently, with an initial indication of some liquid formation near 1568 and 1616°C, with subsequent changes until the entire sample had melted some 100 to 160°C higher than the first indication of melting. This is attributed to the multiphase starting material and/or decomposition of the hercynite iron spinel.

3.3.3 Microstructure

Samples were cut from sibling electrodes and insulators received in the U-02 channel geometry. The samples were vacuum impregnated with resin and polished for microstructural examination. The microstructures are shown in Figures 18 through 31.

FIGURE 18. Microstructure of MgO Insulator-85

FIGURE 19. Microstructure of MgO Insulator-90

FIGURE 20. Microstructure of Graded CeO₂·ZrO₂·Ta₂O₅ Electrode (see also Figures 21 and 22)

FIGURE 21. Microstructures of Graded $\text{CeO}_2\text{-ZrO}_2\text{-Ta}_2\text{O}_5$ Electrode: (a) $0.35\text{CeO}_2 \cdot 0.65\text{ZrO}_2$; (b) $0.5\text{CeO}_2 \cdot 0.5\text{ZrO}_2$; (c) $0.75\text{CeO}_2 \cdot 0.25\text{ZrO}_2$; (d) $0.78\text{CeO}_2 \cdot 0.2\text{ZrO}_2 \cdot 0.02\text{Ta}_2\text{O}_5$

(e)

0.01cm

(f)

0.01cm

FIGURE 22. Microstructures of Graded $\text{CeO}_2\cdot\text{ZrO}_2\cdot\text{Ta}_2\text{O}_5$
Electrode: (e,f) $0.78\text{CeO}_2\cdot 0.20\text{ZrO}_2\cdot 0.02\text{Ta}_2\text{O}_5$

FIGURE 23. Microstructure of $0.5\text{CeO}_2 \cdot 0.5\text{ZrO}_2$ Electrode
(see Figure 24)

FIGURE 24. Microstructure of 0.5CeO₂·0.5ZrO₂ Electrode: Normal and Parallel to the Top Surface of the Electrode

FIGURE 25. Microstructure of $\text{La}_{0.95}\text{Mg}_{0.05}\text{CrO}_3$ (Westinghouse)

FIGURE 26. Microstructures of $\text{LaMg}_{0.05}\text{Cr}_{0.95}\text{O}_3$ Electrode (General Refractories)

FIGURE 27. Microstructure of $0.75 \text{ MgAl}_2\text{O}_4 \cdot 0.25 \text{ Fe}_3\text{O}_4$ Electrode 99 (Battelle-Northwest)

FIGURE 28. Microstructure of $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ Electrode 130 (Battelle-Northwest)

FIGURE 29. Microstructure of $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ Electrode MS-773 (Transtech)

FIGURE 30. Microstructure of $0.75\text{FeAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ (MIT)

FIGURE 31. Microstructure of 0.75 FeAl₂O₄·0.025Fe₃O₄ Electrode (LASL)

3.3.3.1 MgO Insulators

The hot pressed MgO insulators are made up of large, fused MgO crystals, surrounded by MgO fines. The only difference between the MgO-85 (85% density) and the MgO-90 (90% density) appears to be the size and number of the dense MgO particles, Figures 18 and 19. The higher density MgO has more of the larger size particles. Both retain the high percentage of open porosity.

3.3.3.2 Graded $\text{CeO}_2\text{-ZrO}_2\text{-Ta}_2\text{O}_5$ Electrode

The graded $\text{CeO}_2\text{-ZrO}_2\text{-Ta}_2\text{O}_5$ electrode, fabricated at Westinghouse Research Laboratory, was composed of four layers of 0.35 $\text{CeO}_2\text{-0.65 ZrO}_2$, 0.50 $\text{CeO}_2\text{-0.50 ZrO}_2$, 0.75 $\text{CeO}_2\text{-0.25 ZrO}_2$ and 0.78 $\text{CeO}_2\text{-0.20 ZrO}_2\text{-0.02 Ta}_2\text{O}_5$. Although the thickness of each layer varied across the length and width of the electrode, and it is difficult to define precisely the boundaries between layers, the approximate thicknesses are 0.18, 0.11, 0.11 and 0.20 cm, respectively, Figure 20. The 0.35 $\text{CeO}_2\text{-0.65 ZrO}_2$ and 0.5 $\text{CeO}_2\text{-0.5 ZrO}_2$ layers are made up of large particles, 0.008-0.012 cm in diameter, surrounded by fines which have partially sintered, Figures 20 and 21. The 0.35 $\text{CeO}_2\text{-0.65 ZrO}_2$ electrode layer also contains a substantial number of microcracks which are both trans- and intergranular in nature. The 0.5 $\text{CeO}_2\text{-0.5 ZrO}_2$ has sintered to a greater degree although both exhibit a high open porosity.

The higher CeO_2 electrodes, 0.75 $\text{CeO}_2\text{-0.25 ZrO}_2$ and 0.78 $\text{CeO}_2\text{-0.20 ZrO}_2\text{-0.02 Ta}_2\text{O}_5$ layers, although initially made up of larger particles surrounded by fines before sintering, have undergone substantial sintering, although the residual shapes of the larger 0.75 $\text{CeO}_2\text{-0.25 ZrO}_2$ particles can be resolved more clearly, Figures 20, 21(c,d), and 22(e,f). The pores of the 0.78 $\text{CeO}_2\text{-0.20 ZrO}_2\text{-0.02 Ta}_2\text{O}_5$ have become more rounded and uniform in size and shape, with a lower percentage of open porosity.

All of the compositions except the 0.75 $\text{CeO}_2\text{-0.25 ZrO}_2$ appeared to be single phase, with the latter exhibiting a very small amount of darker second phase at the grain boundaries, Figure 21. The composition of this phase was not determined.

3.3.3.3 0.5 $\text{CeO}_2\text{-0.5 ZrO}_2$ Electrode

The 0.5 $\text{CeO}_2\text{-0.5 ZrO}_2$ electrode is composed of larger particles surrounded by fines which have been hot pressed into the electrode geometry, Figures 23 and 24. The microstructures are substantially different, depending upon the orientation relative to the electrode surface. Normal to the surface, the pores and grains are irregular in shape. Long cracks run through and around many of the larger particles and are oriented generally parallel to the electrode surface. In contrast, parallel to the electrode surface, the grains and pores are more uniform in shape, with the cracks shorter in length and oriented in all directions. The electrode is single phase.

3.3.3.4 La(Mg)CrO₃ Electrodes

The hot pressed nominal La_{0.95} Mg_{0.05} CrO₃ (Westinghouse) contains very small smooth pores and a second phase, (Figure 25). The second phase appears to contain larger amounts of chromium and magnesium compared to the matrix, as well as being a sink for the impurities.

The hot pressed nominal La Mg_{0.05} Cr_{0.95} O₃ (General Refractories) also contains a second phase, Figure 26, which is rich in lanthanum and significantly depleted in chromium. The second phase is concentrated primarily at grain boundaries. The pores of this hot pressed material are significantly larger than the other lanthanum chromite and are irregular in shape.

The electron microprobe analysis of the matrices of these show the concentration of the Cr/La to be higher for La_{0.95} Mg_{0.05} CrO₃ than for the La Mg_{0.05} Cr_{0.95} O₃, which is consistent with the chemical analysis (see Table 5).

3.3.3.5 0.75Mg Al₂O₄·0.25Fe₃O₄ Electrodes

The microstructure of the 0.75 Al₂O₄·0.25Fe₃O₄ prepared by Battelle, Pacific Northwest Laboratories (PNL) with controlled porosity are shown in Figures 27 and 28. The spinel is made up of large grains (~0.05 cm in diameter) which contain a uniform distribution of pores. Many of the pores in the grains reflect the crystallographic orientation of the individual grains, e.g., being square or diamond shape. The 0.75Mg Al₂O₄·0.25 Fe₃O₄ (Transtech, Figure 29) is a higher density spinel. The grain size is also large, but the pores are generally spherical. Both 0.75Mg Al₂O₄·0.25 Fe₃O₄ electrodes contain a second phase which is located at the grain boundaries, especially the triple point between grains. This phase is composed principally of the impurities present in the starting powders, i.e., calcium, silicon, barium, with varying amounts of iron and aluminum. None of these impurities are found in the grains of the matrix spinel. The concentration of this second phase is highest in the Transtech electrodes.

3.3.3.6 0.75Fe Al₂O₄·0.25Fe₃O₄ Electrodes

The 0.75Fe Al₂O₄·0.25Fe₃O₄ electrodes were hot pressed at two laboratories, Massachusetts Institute of Technology and Los Alamos Scientific Laboratory, using two different powder compositions. The MIT electrodes was multiphase, (Figure 30). The matrix area was an iron aluminum spinel with the light second phase composed of nearly 100% iron oxide with impurities of aluminum and silicon. The dark second phase is made up of iron and aluminum with major quantities of silicon and potassium and some trace elements. The iron to aluminum ratio of this latter second phase is lower than that of the matrix spinel. The potassium was present in the starting powders.

The LASL hot pressed iron aluminum spinel was hot pressed from a mixture of two different powders, each with apparent different compositions. This spinel is two phase, Figure 31. In addition to the iron spinel second phase, the darker second phase is principally aluminum with small quantities of iron.

3.3.4 Thermal Expansion

The thermal expansion of the reference electrodes was measured from approximately 60 to 1500°C using an aluminum oxide push rod dilatometer. Measurements were made in air at atmospheric pressure. The samples were approximately 1.9 cm long. Heating and cooling rates were linear with temperature rate changes of 4°C/min.

The expansion was measured with a transducer with a resolution of $\pm 2.5 \times 10^{-5}$ cm. The precision of the measurement is of the order of 0.05%. With a similar precision for the measurement of the calibration standard, the overall precision is $\sim 0.1\%$.

The accuracy of the measurements was determined using a tungsten standard (SRM 737) supplied by the U.S. National Bureau of Standards, which is accurate to $\pm 5\%$. Temperatures were measured using a platinum versus platinum-10% rhodium thermocouple, which had been calibrated against a standard platinum resistance thermometer. The accuracy of the temperature measurement in the system is within 5°C. The overall accuracy of the thermal expansion data is estimated to be better than 5%.

The thermal expansion data are illustrated in Figures 32 through 37. The average thermal expansions from 100 to 1400°C calculated from $\Delta L/L$ data are summarized in Table 7. The dimensions of the electrodes before and after the thermal expansion are tabulated in Table 8.

Some of the electrode materials increased in length during heating and cooling. Only small increases in length were observed for the $\text{La}_{0.95}\text{Mg}_{0.05}\text{CrO}_3$ and all $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ electrodes with a very large increase for the $0.75\text{FeAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$. For the latter, a sharp change in $\Delta L/L$ was observed to begin near 1000°C, which corresponds to similar sharp changes in the thermal diffusivity and electrical conductivity.

Thermal expansion data for the graded $\text{CeO}_2 \cdot \text{ZrO}_2$ and $0.5\text{CeO}_2 \cdot 0.5\text{ZrO}_2$ have been reported in the reports describing the US-USSR U-02 Phase I test. (1-3)

3.3.5 Thermal Diffusivity/Conductivity

The thermal diffusivities of the MgO insulators and electrodes were measured using a laser pulse technique from near room temperature to temperatures up to 1750°C. Briefly, this technique consists of heating one

FIGURE 32. Thermal Expansion of $0.75 \text{ MgAl}_2\text{O}_4 \cdot 0.25 \text{ Fe}_3\text{O}_4$ (BNW-99) in Air

FIGURE 33. Thermal Expansion of $0.75 \text{ MgAl}_2\text{O}_4 \cdot 0.25 \text{ Fe}_3\text{O}_4$ (BNW-130) in Air

FIGURE 34. Thermal Expansion of $0.75 \text{MgAl}_2\text{O}_4 \cdot 0.25 \text{Fe}_3\text{O}_4$ Electrode (Transtech - MS-737) in Air

FIGURE 35. Thermal Expansion of $0.75 \text{FeAl}_2\text{O}_4 \cdot 0.25 \text{Fe}_3\text{O}_4$ Electrode (MIT - 4) In Air

FIGURE 36. Thermal Expansion of $\text{La}(\text{Mg}_{0.05}\text{Cr}_{0.95})\text{O}_3$ Electrode (Westinghouse - Reference Hot Pressed) in Air.

FIGURE 37. Thermal Expansion of $(\text{La}_{0.95}\text{Mg}_{0.05})\text{CrO}_3$ Electrode (Westinghouse - Hot Pressed) in Air

**TABLE 7. Coefficient of Thermal Expansion of Electrodes
(100 to 1400°C in Air)**

	$\alpha/^\circ\text{C} (10^{-6})$
$0.5\text{CeO}_2 \cdot 0.5\text{ZrO}_2$	13.2
$0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$	
BNW-99 #1	9.5
#2	9.8
BNW-130 #1	9.7
#2	9.8
TransTech MS-737	9.1
$0.75\text{FeAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ (MIT)	9.0
$(\text{La}_{0.95}\text{Mg}_{0.05})\text{CrO}_3$	
Westinghouse Ref	8.9
Westinghouse U-02	8.7
General Refractories	8.8

TABLE 8. Dimensional Changes of Thermal Expansion Samples

	Length (cm)		Change
	Before	After	
$0.75\text{FeAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$			
130 #1	1.876	1.878	+0.002
#2	1.878	1.883	+0.005
99	1.815	1.815	0.000
MS-737	1.858	1.861	+0.003
$(\text{La}_{0.95}\text{Mg}_{0.05})\text{CrO}_3$ (W)			
reference U	1.916	1.917	+0.001
#7	1.860	1.860	0.000
$\text{La}(\text{Mg}_{0.05})\text{CrO}_3$ (G.R.)	1.881	1.881	0.000
$0.75\text{FeAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ (MIT)	1.909	1.935 ^(a)	+0.026

(a) Sample experienced a 1% increase in weight and microscopic change in appearance with some evidence of melting.

surface of a thin sample disc with a short heat pulse from ruby laser.⁽⁵⁾ The heat pulse passes through the sample and the temperature transient on the back surface of the sample is measured as a function of time. The temperature transient is recorded and the thermal diffusivity determined from the shape of the temperature-versus-time curve and the measured sample thickness. Each sample was heated to the measurement temperature in a tungsten resistance furnace at a slightly positive atmospheric pressure of purified argon. The samples were held in an α -Al₂O₃ holder. Measurements are accurate to $\pm 5\%$.

The thermal conductivity (λ) was calculated from the thermal diffusivity (α), density (ρ), thermal expansion ($\Delta L/L$) and specific heat (C_p) by the equation

$$\lambda = \alpha \cdot \rho \cdot C_p \quad (1)$$

All of the above properties have been measured with the exception of the specific heat. The density at measurement temperature was calculated using the measured room temperature density (ρ_0) and the measured thermal expansion values using the equation

$$\rho = \rho_0 (1 + 3 \Delta L/L)^{-1} \quad (2)$$

The specific heat values were obtained from: 1) reported literature C_p data; 2) calculated values using the Kopp-Neuman Law where the molar C_p of a compound or alloy is equal to the sum of the product of the atomic specific heats of its constituent elements, i.e.

$$C_p = \sum_{i=1}^n x_i (C_p)_i \quad (3)$$

and/or 3) calculations using Debye's expression for C_p at high temperatures. In the latter calculations, the heat capacity at constant volume, C_v , approaches $3R$ above the Debye temperature, θ , or

$$C_v = 5.95 \times (\text{number of atoms/molecule}) \quad (4)$$

However, to calculate the heat capacity at constant pressure, (C_p)

$$C_p = C_v + a^2 VT \beta^{-1} \quad (5)$$

where a is the volumetric coefficient of expansion; V is the molar volume; and β is the compressibility. The compressibility is inversely proportional to the bulk modulus (B) and elastic modulus (E).

$$B = \frac{E}{3(1 - 0.2\nu)} \quad (6)$$

where μ is Poisson's ratio and varies between 0.26 and 0.32. Thus, specific heat can be estimated if E is known as a function of temperature.

The volumetric thermal expansion (a) can be calculated from the measured values of the linear thermal expansion, α

$$a = \frac{\partial V}{\partial T} \bigg|_p V^{-1} = 3 \frac{\partial V}{\partial T} \bigg|_p L^{-1} = 3\alpha \quad (7)$$

Therefore, the biggest unknown in calculating the thermal conductivity from the thermal diffusivity data for the Phase II U-02 materials appears to be the determination of the specific heat.

The specific heat of MgO is known and recommended values were used to calculate the thermal conductivity.

$$C_p = 0.288 + 7.71 \times 10^{-6}T - 4.03 \times 10^{-3}T^{-2} \text{ cal/g-}^\circ\text{C} \quad (8)$$

However, for the $\text{CeO}_2\text{-ZrO}_2$, La(Mg)CrO_3 , $0.75\text{Fe Al}_2\text{O}_4 \cdot 0.25 \text{Fe}_3\text{O}_4$ and $0.75 \text{Mg Al}_2\text{O}_4 \cdot 0.25 \text{Fe}_3\text{O}_4$ electrode materials specific heats were calculated using the Kopp-Neuman law in the temperature range where C_p for the oxides are known. The Debye expression was used to verify these data and to calculate C_p values at the higher temperatures.

3.3.5.1 MgO

The thermal diffusivity/conductivity for MgO-85 was identical to the similar 85% dense insulators used in the U-02 Phase I test, Figure 38 with

$$\lambda = (1.640 \times 0.01155T^\circ\text{C})^{-1} \text{ watts/cm-}^\circ\text{C}^{(3)} \quad (9)$$

The 90% dense MgO-90 insulator had a thermal diffusivity and conductivity ~5% higher than that for the 85% dense MgO up to 1000°C . Above 1000°C , the thermal conductivity of the more dense oxide appeared to approach a constant thermal conductivity of $0.072 \text{ watts/cm-}^\circ\text{C}$.

3.3.5.2 $\text{CeO}_2\text{-ZrO}_2$

The thermal diffusivity of the $0.5 \text{CeO}_2 \cdot 0.5 \text{ZrO}_2$ was the same, within experimental errors as similar $0.5 \text{CeO}_2 \cdot 0.5 \text{ZrO}_2$ (corrected for density) electrodes tested in the U-02, Phase I. The thermal diffusivity measurements for the graded $0.35 \text{CeO}_2 \cdot 0.65 \text{ZrO}_2$, $0.5 \text{CeO}_2 \cdot 0.5 \text{ZrO}_2$, $0.75 \text{CeO}_2 \cdot 0.25 \text{ZrO}_2$, and $0.78 \text{CeO}_2 \cdot 0.20 \text{ZrO}_2 \cdot 0.02 \text{Ta}_2\text{O}_5$ could not be measured. However, the calculated thermal conductivity for the $\text{CeO}_2 \text{ZrO}_2 \text{TaO}_5$ electrode materials are tabulated in Table 9 and compared in Figure 39.

FIGURE 38. Thermal Resistivities of MgO Insulators

FIGURE 39. Thermal Conductivities of MHD Electrode Materials

TABLE 9. Calculated Thermal Conductivity for CeO₂ ZrO₂ Electrodes (Watts/cm°C)

Temperature, K	0.12 Y ₂ O ₃ 0.88 ZrO ₂	0.18 CeO ₂ 0.82 ZrO ₂	0.50 CeO ₂ ^(a) 0.50 ZrO ₂	0.50 CeO ₂ ^(a) 0.50 ZrO ₂	0.75 CeO ₂ 0.25 ZrO ₂	0.78 CeO ₂ 0.20 ZrO ₂ 0.02 Ta ₂ O ₃
	(Y-13)	(C-2-15)	I (C-3-22)	II (C-3-22)	(C-4-19)	(C-5-9)
400	0.0124					
500	0.0127					
600	0.0127					
700	0.0125					
800	0.0123	0.0151	0.0118	0.0117	0.0158	0.0187
850						
900	0.0120	0.0148	0.0115	0.0114	0.0152	0.0183
1000	0.0119	0.0143	0.0113	0.0111	0.0147	0.0177
1050						0.0175
1100	0.0119	0.0140	0.0112	0.0109	0.0144	0.0174
1150					0.0144	0.0172
1200	0.0120	0.0138	0.0110	0.0106	0.0144	0.0168
1250					0.0140	0.0161
1300	0.0121	0.0137	0.0109	0.0103	0.0133	0.0154
1350	0.0124	0.0137			0.0126	
1400	0.0127	0.0137	0.0105	0.0100	0.0121	0.0148
1450	0.0129	0.0138			0.0116	
1500	0.0129	0.0139	0.0101	0.00951	0.0111	0.0142
1550	0.0129	0.0141				
1600	0.0127	0.0145	0.00964	0.00899	0.0103	0.0137
1650	0.0126	0.0147				
1700	0.0127	0.0152	0.00932	0.00862	0.00973	0.0131
1750	0.0129	0.0159				
1800	0.0132	0.0162	0.00912	0.00837	0.00953	
1850		0.0174				
1900	0.0139	0.0187	0.00879	0.00801	0.00950	

(a) The thermal conductivities were calculated using two different values for C_p which vary at high temperatures. The values for I are considered most reliable.

The unusual shapes of the λ^{-1} versus T curves also preclude the generation of the usual simple linear expression for λ^{-1} except that for the 0.5 CeO₂·0.5 ZrO₂ electrode, Figure 40. However, the data for 0.5 CeO₂·0.5 ZrO₂ can be separated into two linear portions, with the break at 1370°K. The linear equations are

$$\lambda = (66.52 + 0.02151 T)^{-1} \text{ watts/cm-}^\circ\text{C} [500 - 1370^\circ\text{K}] \quad (10)$$

and

$$\lambda = (34.29 + 0.04769 T)^{-1} \text{ watts/cm-}^\circ\text{C} [1370 - 1900^\circ\text{K}] \quad (11)$$

FIGURE 40. Thermal Resistivity of $0.5\text{CeO}_2 \cdot 0.5\text{ZrO}_2$ Electrode (Phase I)

3.3.5.3 $0.75\text{Mg Al}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$

The thermal diffusivity and conductivity of three $0.75\text{Mg Al}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ spinel electrodes (BNW) were measured to near 1500°C . These data are shown in Figures 41 and 42. Although fabricated using the same method but with different starting powders, (a) the data for the three samples are slightly different. The thermal conductivities for the BNW-83 and the BNW-130 spinel electrodes can be expressed as

$$\lambda = 27.2 \pm 0.0128T \text{ watts/cm-}^\circ\text{C} \quad (12)$$

and

$$\lambda = 29.3 \pm 0.00964T \text{ watts/cm-}^\circ\text{C} \quad (13)$$

respectively.

The BNW-0 was a higher density (95% TD) sample with a reproducible inflection near 560°C . This was not observed for the final electrode materials.

(a) BNW-83 was fabricated using KE powder and BNW-130 was fabricated using KO powder (Table 1).

FIGURE 41. Thermal Diffusivity of $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25 \text{Fe}_3\text{O}_4$

FIGURE 42. Thermal Resistivity of $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$

3.3.5.4 $0.75 \text{ Fe Al}_2\text{O}_3 \cdot 0.25 \text{ Fe}_3\text{O}_4$ (MIT)

The thermal diffusivity of the hot pressed $0.75 \text{ Fe Al}_2\text{O}_3 \cdot 0.25 \text{ Fe}_3\text{O}_4$ (MIT) exhibited changes on heating and cooling, Figure 43. These values are compared with a hercynite-hematite sintered in air. The latter exhibited large decreases in diffusivity on heating between 1200 and 1200°C when measured in inert argon gas with a very low oxygen pressure. On cooling, the diffusivity remained low, and was very close to that of the hot pressed electrode material.

Large changes have also been observed in the thermal expansion and electrical conductivity data in this same temperature range. This electrode material is not single phase and is susceptible to changes in microstructure and valence resulting from oxygen pressure changes such as that which occurred when the air-sintered hercynite-magnetite was heated in a low-oxygen inert gas.

Because of the multiphase composition and changes due to oxygen pressure variations, the thermal conductivity is difficult to calculate. However, for the hot pressed (MIT) $0.75 \text{ Fe Al}_2\text{O}_3 \cdot 0.25 \text{ Fe}_3\text{O}_4$, the calculated thermal conductivity increases linearly with temperature from $\sim 0.0213 \text{ watt/cm}^\circ\text{C}$ at 200°C to $\sim 0.0240 \text{ watt/cm}^\circ\text{C}$ at 1050°C , then remains nearly constant at higher temperatures. However, there are large uncertainties in these data because of the multiphases and apparent changes on heating.

FIGURE 43. Thermal Diffusivity of $0.75 \text{ Fe Al}_2\text{O}_3 \cdot 0.25 \text{ Fe}_3\text{O}_4$

3.3.5.5 La (Mg) CrO_3

The thermal diffusivities and thermal conductivities for the nominal compositions $\text{La}_{0.95}\text{Mg}_{0.05}\text{CrO}_3$ and $\text{La Mg}_{0.05}\text{Cr}_{0.95}\text{O}_3$ are illustrated in Figures 44 and 45. The values for the two different chromites are approximately the same except at the lower temperatures where the $\text{La}_{0.95}\text{Mg}_{0.05}\text{CrO}_3$ is approximately 10% higher than the $\text{La Mg}_{0.05}\text{Cr}_{0.95}\text{O}_3$. The thermal conductivities fit a $\lambda = (A + BT)^{-1}$ equation from 100 to 1050°C, Figure 46.

$$\lambda = (27.87 + 0.02133T)^{-1} \text{ watts/cm-}^\circ\text{C} \text{ (La}_{0.95}\text{Mg}_{0.05}\text{CrO}_3) \quad (14)$$

$$\lambda = (30.6 + 0.01891T)^{-1} \text{ watts/cm-}^\circ\text{C} \text{ (La Mg}_{0.05}\text{Cr}_{0.95}\text{O}_3) \quad (15)$$

Above 1050°C the thermal conductivity exhibits a reversible inflection, with a minimum near 1250°C.

For engineering purposes, a third order equation can be used to fit the data, although it does not fit precisely above 1050°C.

$$\lambda = 0.0372 - 2.82 \times 10^{-5} T + 1.14 \times 10^{-8} T^2 \text{ watts/cm-}^\circ\text{C}$$

$$\text{La}_{0.95}\text{Mg}_{0.05}\text{CrO}_3 \quad (16)$$

$$\lambda = 0.0321 - 1.87 \times 10^{-5} T + 7.13 \times 10^{-9} T^2 \text{ watts/cm-}^\circ\text{C}$$

$$\text{La(Mg}_{0.05}\text{)Cr}_{0.95}\text{O}_3 \quad (17)$$

FIGURE 44. Thermal Diffusivity of $\text{La}_{0.95}\text{Mg}_{0.05}\text{CrO}_3$ (Westinghouse)

FIGURE 45. Thermal Conductivities of $\text{La}(\text{Mg})\text{CrO}_3$ [Curves Represent Equations (16) and (17)]

FIGURE 46. Thermal Resistivity of $\text{La}(\text{Mg})\text{CrO}_3$

4.0 WORK ANTICIPATED DURING NEXT QUARTER

4.1 ELECTROCHEMICAL EFFECTS OF POTASSIUM SEED

The testing and evaluation of seed/slag in a dc electric field on MHD electrodes and insulators will continue. Work will emphasize the improvement of the testing procedures and equipment and further testing of electrodes and insulators as functions of temperature seed concentration, and current density. Efforts will continue to relate results to results of other MHD testing. Studies to determine the effects of seed in slags will be initiated.

4.2 ELECTRODE-INSULATOR DEVELOPMENT

The fabrication of hot pressed, refractory capped electrodes by a commercial supplier will be completed. Testing, characterization, and evaluation of these electrodes in the MIT MHD facility will be initiated. Development of graded electrode configurations will continue.

4.3 CHARACTERIZATION AND EVALUATION

The post-test characterization and evaluation of the electrodes and insulators from the US Materials Phase II test in the USSR U-02 will be completed. The characterization and evaluation of the materials relating to the U-25 electrode crack program will continue, especially those relating to thermal physical properties of the electrodes and insulator materials.

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